A STUDY OF ELASTIC SCATTERING AND DEACTIVATION OF METASTABLE NITROGEN MOLECULES

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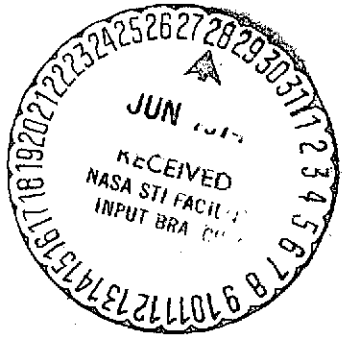

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16. Abstract

The differential scattering of fast beams of nitrogen molecules on various targets has been studied. Anomalous behavior has been noted for the scattering of metastable molecules, which is connected with the quenching process. Scattering data have been used to determine anisotropic reaction potential parameters for the systems studied, in the range 0.1 - 50 eV. A quenching scheme via dissociation of the excited molecule is proposed. A calculation of the scattering pattern has been made in the classical approach which agrees with the measurements.

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A STUDY OF ELASTIC SCATTERING AND DEACTIVATION OF METASTABLE NITROGEN MOLECULES

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Study of collisions of metastable particles presents interest because /3* of their important role in processes which occur in the upper layers of planetary atmospheres, in the physical and chemical kinetics of plasmas, and the like.

In the present work, preliminary results of which were described in reference 1, the method of scattering of fast beams at low angles has been used to study interaction forces and the deactivation mechanism of metastable ($E^3\Sigma^+g$) N_2 molecules in collisions with various partners (Ar, N_2, O_2, CO_2) in the ground state.

1. The study of differential scattering was performed on the modified set-up described in reference. 2. The charge exchange block, the system for admitting the scattering gas, and the recording system were subjected to modernization. The charge exchange chamber is a furnace with a controllable temperature and permits the use of either stable gases or alkali metal vapors for charge exchange.

Charge exchange in Cs vapor was used to obtain a beam of metastable N_2 molecules. In the work of Kalinin et al., [1] it was incorrectly assumed that for charge exchange on Cs the metastable $A^3\Sigma^+\mu$ state ($C^3\pi$ $A^3\Sigma^*\mu$) is the /4 final one. However, the relative location of the terms for the N_2^+ ion and N_2 molecule (see Figure 1 and also Table 1) ensures a minimum resonance defect in the case of Cs for charge exchange into the metastable $E^3\Sigma^+g$ state (lifetime about 0.2μ sec [3]). The population of the states in the beam can be estimated on the basis of the theory of charge exchange of molecules of Smirnov [4]; rigorous calculations have not been performed in the present work. The large

*Numbers in the margins indicate pagination in the foreign text.

value of the charge exchange section the $E^8\Sigma g$ state (and consequently the predominant population of this state in the beam) is ensured not only by the previously mentioned smallness of the resonance defect, but also by the closeness of the internuclear distances in the N_2 ($E^8\Sigma^+ g$) ion formed by electron impact (see reference 5).

For detection we used an open electron multiplier with a continuous dynode of the (KU) channel type. The high amplification coefficient (about 10^8) and small dimensions of the KU made it possible, by using the discrete calculation technique, to considerably improve the angular resolution of measurements. The characteristic resolving power of a detector for an angle α is $f_\alpha(\theta)$, the efficiency of recording particles scattered into the solid angle around θ. A means of finding $f_\alpha(\theta)$ is described in reference 6, and in the present work it was calculated for a new geometry; the $f_\alpha(\theta)$ function connects up in a simple way the differential scattering section, $\delta(\theta,E)$ with the measured flux of scattered particles, $I(\alpha)$ [6].

The interaction of the systems studied is not spherically symmetrical and the relationship given in reference 6 for $I(\alpha)$ should be modified. Since, for the experimental conditions, the characteristic times for vibrational and rotational movements of molecules are much greater than the characteristic reaction time, the steric orientation of the molecules, $\Omega = \{\phi,\chi,\psi\}$, can be considered "frozen" during the course of the whole collision. For a fixed orientation Ω one can introduce the concept of a differential scattering section into a unit solid angle. /5

$$\delta(\theta,E) = \left[\frac{b}{\sin\theta}\left|\frac{db}{d\theta}\right|\right]_{\Omega,E}.$$

Here θ is the angle between the asymptotes to the initial and final relative velocities; for $\delta(\theta,E)$ a cylindrical symmetry is maintained; that is, with allowance for averaging with respect to orientations, $I(\alpha)$ can be represented by the expression

$$I(\alpha) = B\int_{(\Omega)}\int_{(\theta)}\delta(\theta,\Omega)\, f_\alpha(\theta)\sin\theta d\theta d\Omega = B\int_{(\Omega)}\int_{(b)} b f_\alpha(\theta) db d\Omega, \quad (I)$$

where B is a known constant [6].

Direct inversion of expression (1), that is, obtaining the deviation function $\theta(b,\Omega)$ is not possible, and the most reasonable means of solving the

reverse problem of scattering is matching the measured and calculated dependences of $I(\alpha)$ for the selected potential energy surface (PBS). It is this method that has been used in the present work.

2. Investigation of the differential scattering of N_2 ($E^3\Sigma^+g$) molecules (and also of N_2 molecules in the $X^1\Sigma^+g$ ground state) was carried out at a beam energy E = 2000 eV, in the angle range $\Delta\alpha = 2 \times 10^{-3}$ to 4×10^{-2} radians. The corresponding range of laboratory scattering angles, $\Delta\theta$, defines the range of the interaction energies studied, ΔV = 0.1 to 50 eV. In Figure 2 we show the measured angular distributions of the flux of scattered particles by the continuous lines (typical scatter of measured values is shown by the vertical strokes). It is evident that, in distinction from the case of collision of molecules in the ground state, the scattering of metastable molecules is characterized by clearly expressed special features.

The experimental dependences of $I(\alpha)$ (Figure 2) are potential sources of information about the interaction forces and details of the mechanism of an inelastic process. The problem consists in extracting the indicated information, and further discussion is devoted to this. /6

As the anisotropic potential energy surface, we used the additive potential $V(R,\Omega) = \Sigma_{ij} V(rij)$. Here $V(rij)$ is the interatomic repulsion potential, which is identical for all pairs of atoms of the interacting molecules, molecules, and $V(r) = A \exp(-\beta r)$. Depending on orientation, the deviation function $\theta(b,\Omega)$ was found as described in reference 7. The value of $I(\alpha)$ was calculated from expression (1) by the Monte Carlo method with a statistical accuracy of 3%, which required the realization of up to 10^4 random trajectories. In determining the parameters A and β, along with $I(\alpha)$ we also calculated the value of the integral section, Q (2000), (which was also measured); therein we used formula (1) and the function $1 - f(\theta)$ [6].

In Figure 2, a typical case of matching the dependences of $I(\alpha)$ is shown by the points for the system $N_2(X'\Sigma^+g)$ - $(X'\Sigma^+g)$; in Table 2 we gave values of the parameters A and β as found from the matching for this system. In the same place we give values for the parameters $\bar{A}$ and $\bar{\beta}$ for the exponential approximation of the anisotropic potential averaged with respect to orientations.

3. Now we examine the problem of calculating the pattern of scattering of metastable $N_2(E^3\Sigma^+g)$ molecules. In this calculation it is necessary to reproduce both the path of $I(\alpha)$ and also the position and amplitude of emission.

It is characteristic that the angular position of the anomaly is practically identical for all the systems studied. The amplitude and position $(\theta \sim \frac{V}{E})$ of the observed peak and its presence in the case of the system $N_2(E\varepsilon\Sigma^+g)$ - Ar exclude the possibility of explaining the effect by rainbow scattering. It is natural to associate with the breakdown process of a metastable state.

Calculations of the deviation function $\theta(b,\Omega)$ also give values of W, the energy of relative motion of N atoms in the scattered N_2 $(E^8\Sigma^+g)$ molecule. If /7
W proves to be close to or larger than the dissociation energy D, then breakdown of the fast molecule will be possible. However, it is evident that, for example, for the case of the parameters of the $N_2(X^1\Sigma^+g)$ - N_2 system and the most favorable orientation, conditions for direct breakdown of the $E^3\Sigma^+g$ state are attained only at very small target distances ($b < 1.5$ Å). Hence it follows that the contribution of a direct breakdown mechanism for the excited state can be neglected. The localization of the peak detected indicates a rather sharp "switch-on" of the breakdown probability of the metastable state, which is fully explainable within the framework of the concept of quasi-intersection of the corresponding potential energy surfaces. A quantitative picture of the intersections of terms is shown in Figure 3a, where the alternative possibilities correspond to deactivation by transition of the metastable (fast) particle either into a higher (2-2' shift) or into a lower (3 - 3' shift) excited state. In the latter case the transition is accompanied by a transfer of internal excitation energy into recoil energy; in principle the appearance of the observed blip in the $I(\alpha)$ dependence could be explained by this effect.

The possibility in principle has been investigated quantitatively. If one considers the rule of total spin preservation, then from a diagram of the type of Figure 1 it is evident that the maximum value of the recoil energy [1] does not exceed $q = 8$ eV. Approximating the interacting molecules by point centers, the scattering pattern with crossing of an intersection point can be considered on the basis of the known formalism of Matsuzawa [8]. Neglecting

the interference terms, for the measured total section we can write $\delta_{meas}(\theta) = \delta_{el}(\theta) + \delta_{kv}(\theta)$, where δ_{el} and δ_{kv} are determined by the differential scattering section $\delta_i(\theta)$ for the four possible trajectories upon intersection and the possibility of transition upon one-time passage of the intersection point. Calculations of the partial sections $\delta_i(\theta)$ which were performed showed that for q = 8 eV, on varying the path of the 3 - 3' and 1 - 1' terms and the value of the probability, it is not possible to reproduce simultaneously the position and amplitude of the measured peak. Hence the conclusion was drawn that the deactivation scheme via a lower energy state does not agree with observations and should be rejected (the agreement for this scheme in reference 1 was attained at the expense of an artificial, too high value for the recoil angle, that is, of q). /8

4. A quantitative description of the observed effect (Figure 2) proves simple if the excited state corresponding to the 2 - 2' term (Figure 3) at an internuclear distance R_{int} at the moment of the transition is characterized by repulsion. The repulsion energy, $V(R_{int})$ determines the pulses, $\vec{P}_{org}$ ($|\vec{P}_{org}| = \sqrt{V(R_{int})M}$) of atoms which scatter along the connecting line in the molecule. The scheme used above to calculate $\theta(b,\Omega)$ is well adapted for finding the divergence angles of atoms, θ_1 and θ_2, which are obtained as a result of vector composition of a recoil pulse, $\vec{P}_{org}$ and a pulse caused by interaction of atoms, $\vec{P}_{jRe}$

$$I(\alpha) = B\{\int_{(\Omega)}\int_{(b)}[1 - p(b)]bf_\alpha(\theta_e)dbd\Omega + \int_{(\Omega)}\int_{(b)}p(b)f_\alpha(\theta_1)dbd\Omega + \int_{(\Omega)}\int_{(b)}p(b)f_\alpha(\theta_2)dbd\Omega\}.$$

Here p(b) is the probability of transition (a stipwise function which does not depend on orientation), and θ_{el} is the angle associated with elastic scattering by an additive potential (1 -1') with parameters A and β.

By virtue of the condition of preservation of total spin, the candidates for the role of the indicated state are the $D^3\Sigma^+\mu$ and $^3\Delta g$ states of the N_2 molecule (for $D^3\Sigma^+\mu$ there is some information about the term path[9]; there is none for $^3\Delta g$). Since the paths of the $D^3\Sigma^+\mu$ and $^3\Delta g$ terms are somewhat /9

undefined, the quantity $V(R_{int})$ was the calculation parameter ($V(R_{int}) = 0.6$ eV); the divergence angle for a shift with respect to a 2 - 2' term was taken as equal to 0.8 times the angle for the 1 -- 1' term; the 20% decrease takes account of the difference in asymptotic energies of the intersecting terms (Figure 3a). By varying the values of the parameters A and β, the probability p, and the position of the point of intersection, b_n, it is possible to reach good agreement of measurements with calculation. In Figure 2, we show by points the results of calculating $I(\alpha)$ for the values of the parameters A, β, p, and b_n which are given in Table 2. The statistical accuracy was also equal to about 3%, and the number of random trajectories, to about 10^4. A quantitative agreement of the $I(\alpha)$ measurements, $Q_{meas}(2000)$, and calculation is present for all systems, which serves as support for the correcness of the model chosen.

The model used naturally explains the coincidence of the angular emission positions in $I(\alpha)$ for the various systems -- the main contribution to the deviation of deactivated particles is brought about by a breakdown of the $N_2(E^3\Sigma^+g)$ molecule which is independent of the nature of the partner.

The following is a summary of the basic results of our work:

1. Differential scattering of fast beams of $N_2[(E^3\Sigma^+g), (X^1\Sigma^+g)]$ molecules on various targets has been studied. An anomalous behavior has been observed for the scattering of metastable molecules, which is connected with the quenching process.

2. Scattering data have been used to determine the parameters of anisotropic interaction potentials of the studied systems in the range 0.1 - 50 eV.

3. A quenching scheme via dissociation of the excited molecule is proposed; a calculation of the scattering pattern in the classical approach has been made, which agrees with measurements.

TABLE 1.

$v \rightarrow v'$	$E^3\Sigma_g^+$	$C^3\Pi_u$
0 - 0	-0,190	+0,090
I - 0	+0,085	+0,960
0 - I	-0,450	+0,440
I - I	-0,179	+0,710
2 - 0	+0,853	+I,280
2 - I	+0,091	+0,980

Note: Commas indicate decimal points.

TABLE 1. Energy Defect, δ_E, Equal to Ionization Potential of N_2 Minus Ionization Potential of Cs in Charge Exchange on Cs for Various Vibrational Levels, V, V' of the Ion $N_2^+(X^2\Sigma^+g)$ and the Molecule N_2 in the States $E^3\Sigma^+g$ and $C^3\pi u$.

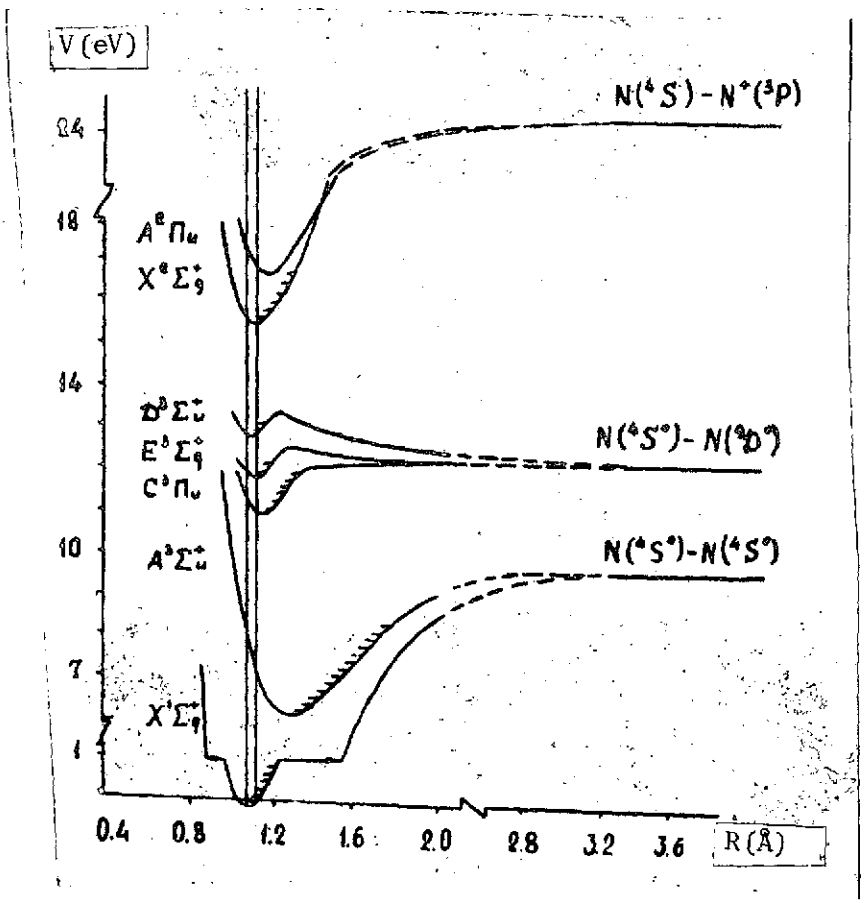
TABLE 2.

System	β, Å^{-1}	A, keV	$\bar{\beta}$, Å^{-1}	$\bar{A}$, keV	p	b_n, Å
$N_2(C^3\Pi_u)-N_2$	3,27	0,367	3,16	2,29	-	-
$N_2(E^3\Sigma_g^+)-N_2$	4,00	0,500	3,55	2,76	0,3	I,85
$N_2(E^3\Sigma_g^+)-O_2$	3,50	0,200	3,12	0,93	0,4	I,85
$N_2(C^3\Pi_u)-CO_2$	3,30	0,400	3,26	3,98	0,2	2,00
$N_2(E^3\Sigma_g^+)-Ar$	4,50	2,500	4,48	I0	0,2	I,70

Note: Commas indicate decimal points.

TABLE 2. Values of Interatomic and Averaged Potential Parameters, Transition Probability p, and Position of Intersection Point, b_n, for Systems Studied.

FIGURE 1.


V (eV)
24
18
14
10
7
1
$A^2\Pi_u$
$X^2\Sigma_g^+$
$D^3\Sigma_u^+$
$E^3\Sigma_g^+$
$C^3\Pi_u$
$A^3\Sigma_u^+$
$X^1\Sigma_g^+$
$N(^4S) - N^*(^3P)$
$N(^4S^o) - N(^2D^o)$
$N(^4S^o) - N(^4S^o)$
0.4
0.8
1.2
1.6
2.0
2.8
3.2
3.6
R(Å)

/12

FIGURE 2.

/13

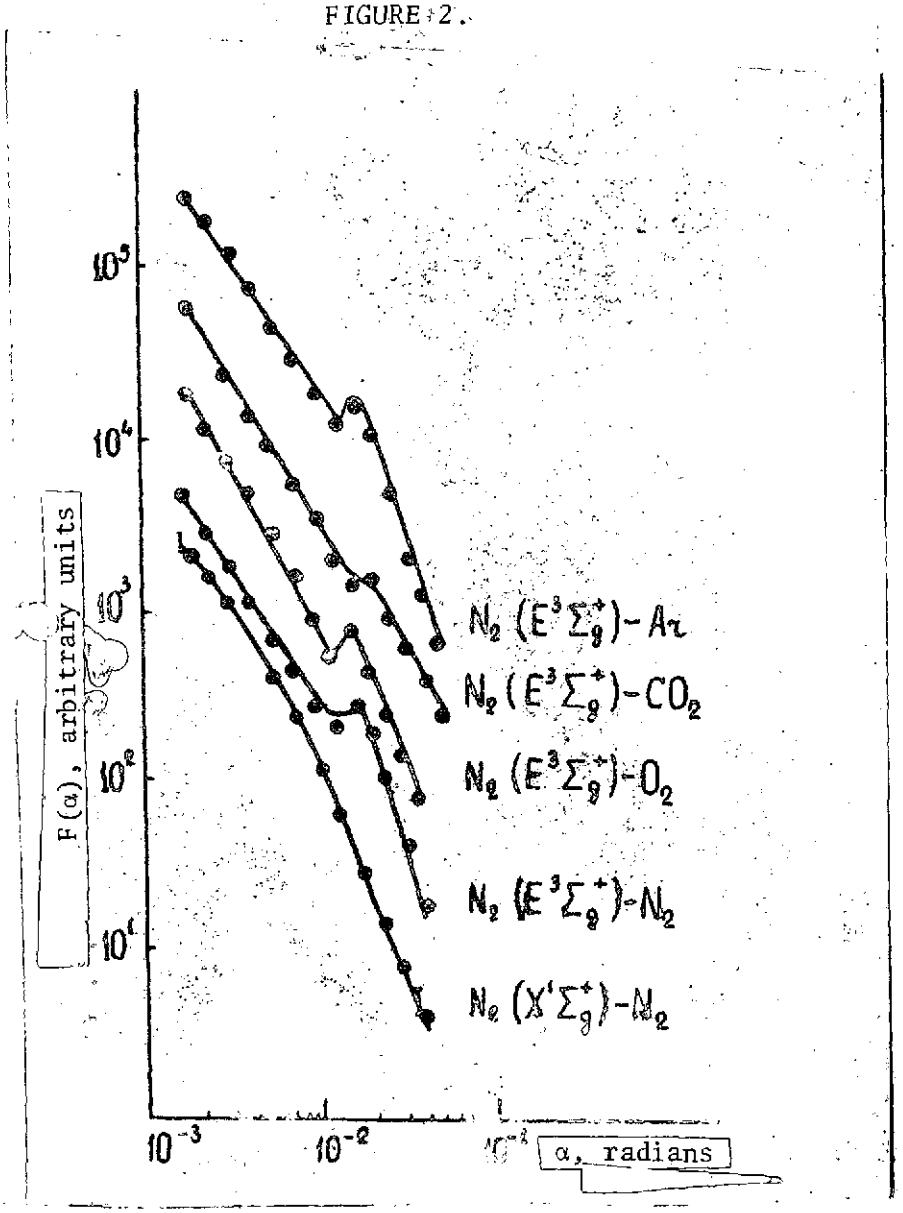
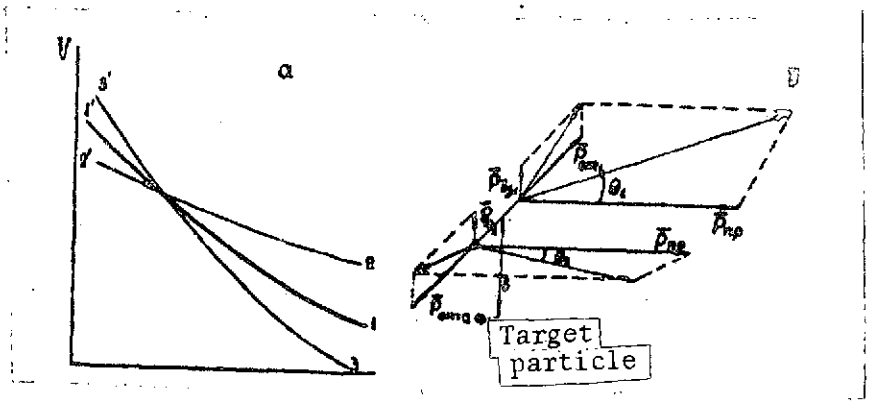

F(α), arbitrary units
10⁵
10⁴
10³
10²
10¹
10⁻³
10⁻²
α, radians
N₂ (E³Σg⁺)-Ar
N₂ (E³Σg⁺)-CO₂
N₂ (E³Σg⁺)-O₂
N₂ (E³Σg⁺)-N₂
N₂ (X¹Σg⁺)-N₂

FIGURE 4.



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